

# Beer's Law Example

This example shows how to compute an extinction coefficient  $k_\lambda$  at a given wavenumber  $\lambda$  using absorbance spectra  $A_\lambda$  of known concentrations  $c$ . The Beer's law relationship is  $ck_\lambda = A_\lambda$ .

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## The Data

Load the napalm data.

```
clearvars
load pnnl_napalm_data
whos
```

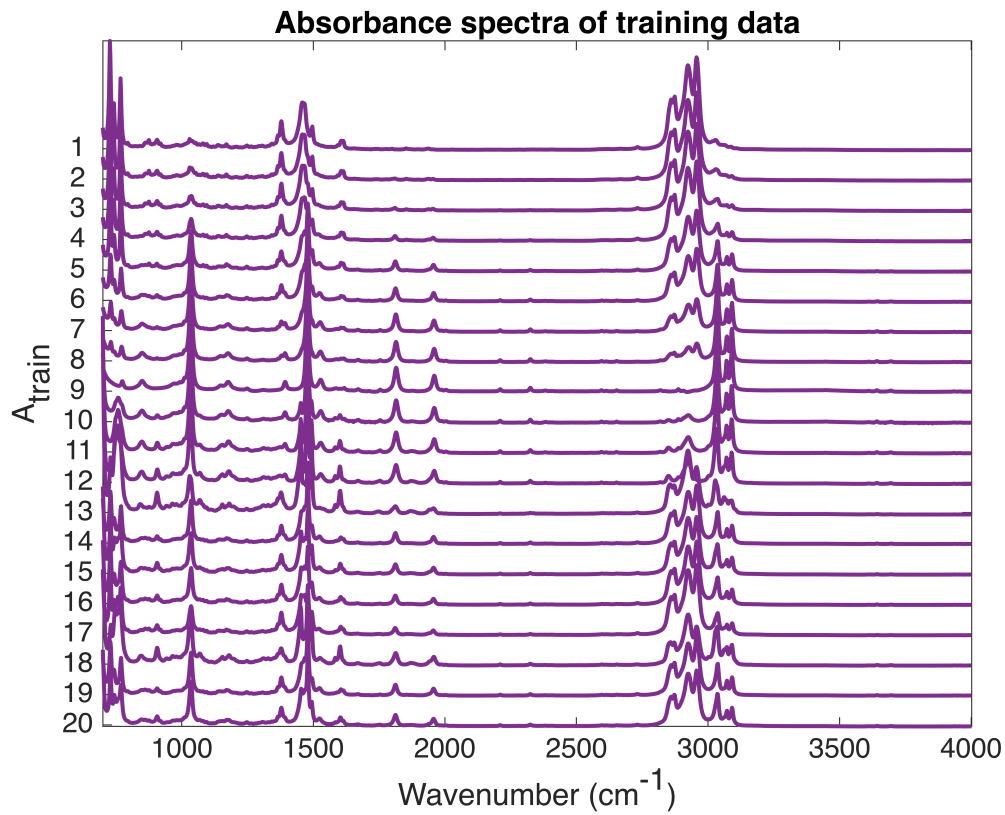
Name	Size	Bytes	Class	Attributes
A_train	20x1713	274080	double	
A_unknown	12x1713	164448	double	
C_train	20x3	480	double	
C_validation	12x3	288	double	
ConcentrationUnits	1x4	8	char	
ConstituentNames	1x3	364	cell	
WavenumberLabel	1x20	40	char	
Wavenumbers	1x1713	13704	double	
ans	1x1	8	double	

The concentration matrix  $C_{\text{train}}$  contains the percent by weight of each of 20 solutions in the training data. The columns correspond to benzene, polystyrene, and gasoline.

$$C_{\text{train}} = \begin{array}{c} \begin{array}{ccc} \textit{benzene} & \textit{polystyrene} & \textit{gasoline} \end{array} \\ \left[ \begin{array}{ccc} 0 & 0 & 100.0000 \\ 5.1309 & 0 & 94.8691 \\ 10.0660 & 0 & 89.9300 \\ 20.1799 & 0 & 79.8201 \\ 40.0120 & 0 & 59.9878 \\ 59.9972 & 0 & 40.0028 \\ 79.8412 & 0 & 20.1588 \\ 89.8273 & 0 & 10.1727 \\ 100.0000 & 0 & 0 \\ 90.0264 & 9.9736 & 0 \\ 80.1375 & 19.8625 & 0 \\ 64.9950 & 35.0005 & 0 \\ 21.0228 & 45.9197 & 33.0575 \\ 49.9507 & 5.0599 & 44.9895 \\ 40.0182 & 20.0385 & 39.9433 \\ 40.0154 & 10.0036 & 49.9810 \\ 30.0059 & 10.0282 & 59.9659 \\ 40.0340 & 39.9670 & 19.9990 \\ 49.9393 & 3.3748 & 46.6859 \\ 46.6501 & 13.4658 & 39.8840 \end{array} \right] \begin{array}{l} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \end{array} \end{array}$$

The absorbance spectra for each of the 20 solutions in the training data are the rows of  $A_{\text{train}}$ .

pnnl\_napalm\_plot\_training\_spectra

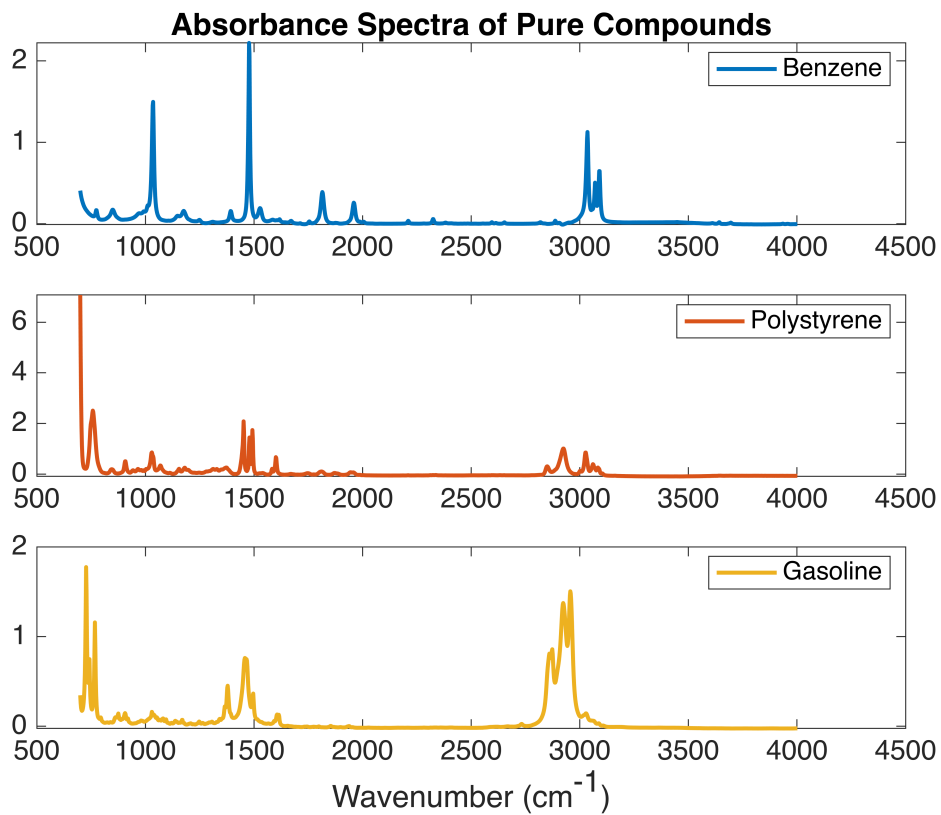


## Pure Spectra

Look at the rows of  $C_{\text{train}}$  and you can see that row 9 is pure benzene and row 1 is pure gasoline. A pure spectra of polystyrene is inferred from a combination of rows 12 and 9.

$$C_{\text{train}}([1, 9, 12], :) = \begin{array}{c} \begin{array}{ccc} \text{benzene} & \text{polystyrene} & \text{gasoline} \end{array} \\ \begin{bmatrix} 0 & 0 & 100.0000 \\ 100.0000 & 0 & 0 \\ 64.9950 & 35.0005 & 0 \end{bmatrix} \end{array} \begin{array}{l} 1 \\ 9 \\ 12 \end{array}$$

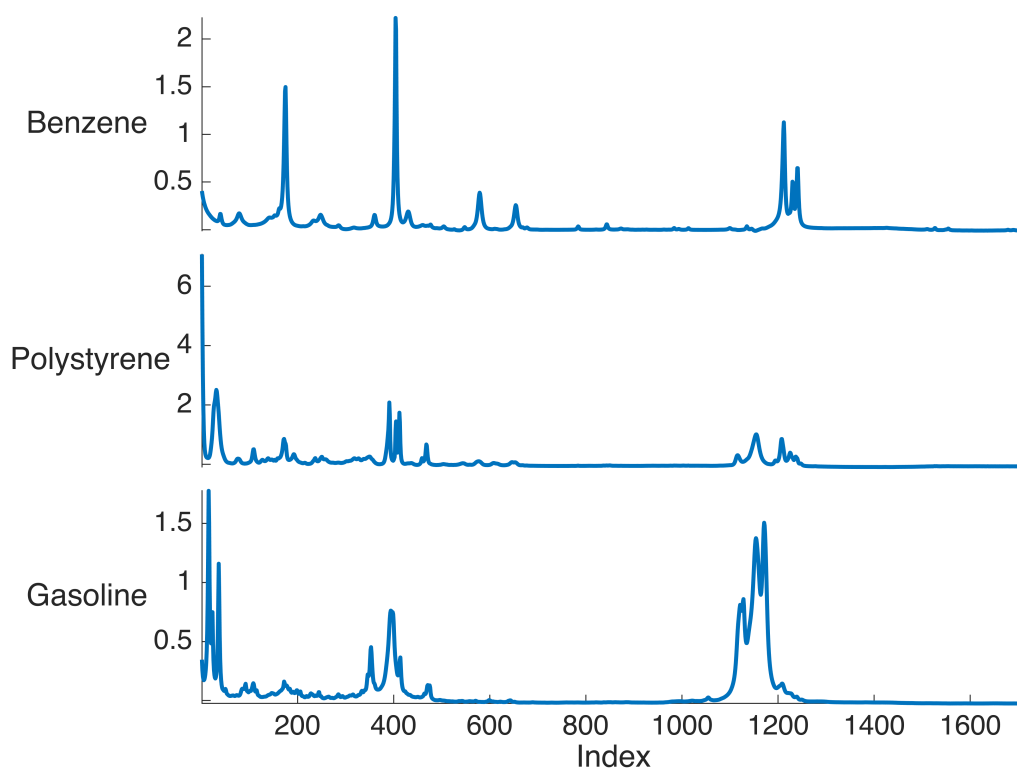
```
A_pure = pnnl_napalm_pure_spectra;
pnnl_napalm_plot_pure_spectra
```



## Locate the best index for benzene

Plot the absorbances with  $1:m$  as the x-axis so you can find the index that corresponds to the best peak for each of the constituents.

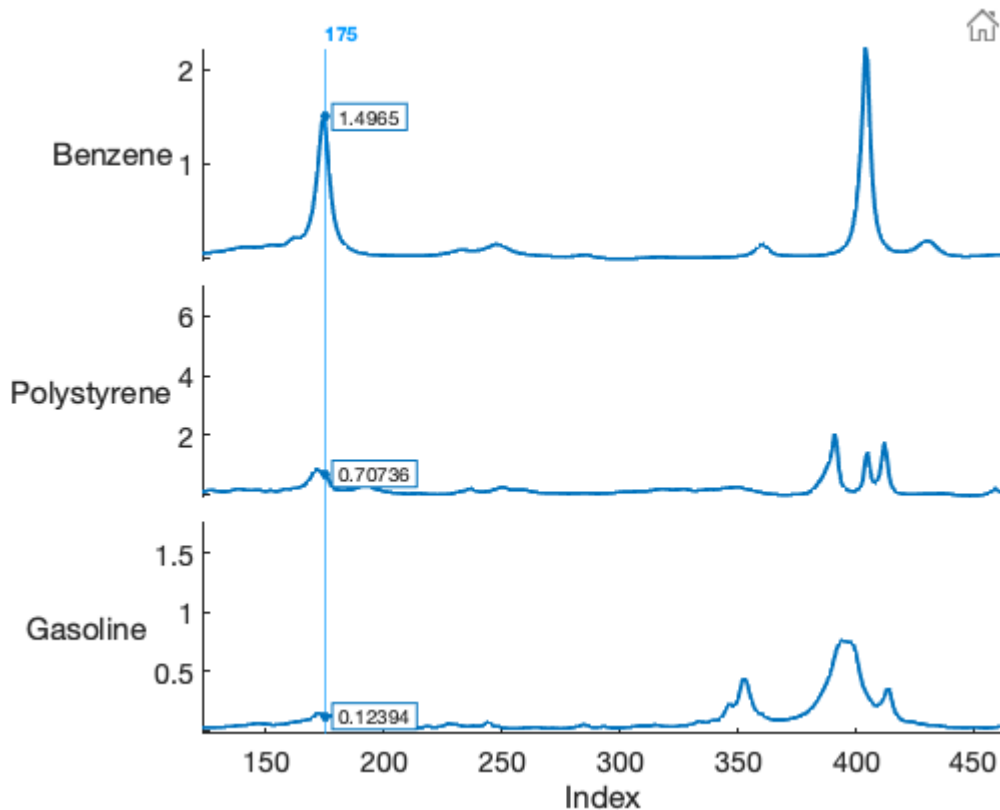
```
m = size(A_pure,2);
figure
stackedplot(1:m,A_pure', 'LineWidth',2, 'FontSize',14, 'DisplayLabels',ConstituentNames);
xlabel('Index')
```



Hover over the plot to examine the peaks of the benzene spectrum. The largest peak in the benzene spectrum seems like the natural one to choose, but there are peaks in the other spectra coinciding with the largest peak, so choose the second largest peak to examine. It has index 175. This corresponds to wavenumber  $\lambda_{175} = 1035.587$ .

```
index = 175;  
lambda = Wavenumbers(index)
```

```
lambda = 1.0356e+03
```



## Beer's Law for Benzene

Pull out the concentration column for benzene and the absorbtion column for  $\lambda_{175} = 1035.587\text{cm}^{-1}$ .

```
c_benzene = C_train(:,1);
A_lambda = A_train(:,index);
```

Compute the extinction coefficient  $k_{\lambda_{175}}$  for benzene for wavenumber  $\lambda_{175} = 1035.587\text{cm}^{-1}$  that best fits the following equation. The fit won't be exact because, for example, looking at the first row there is no value that makes  $0 \cdot k_{\lambda_{175}} = 0.1239$  true. However, we can compute a value for  $k_{\lambda_{175}}$  that minimizes the sum of squares of the difference  $c_{\text{benzene}} \cdot k_{\lambda_{175}} - A_{\lambda_{175}}$  (hence the name "least squares").

$c_{\text{benzene}}$	$A_{\lambda_{175}}$
0	0.1239
5.1309	0.1801
10.0660	0.2207
20.1799	0.3423
40.0120	0.6381
59.9972	0.8222
79.8412	1.1272
89.8273	1.3174
100.0000	1.4965
90.0264	1.4311
80.1375	1.3286
64.9950	1.2203
21.0228	0.5492
49.9507	0.6973
40.0182	0.6603
40.0154	0.5863
30.0059	0.4573
40.0340	0.8525
49.9393	0.6905
46.6501	0.7131

$k_{\lambda_{175}} \approx$

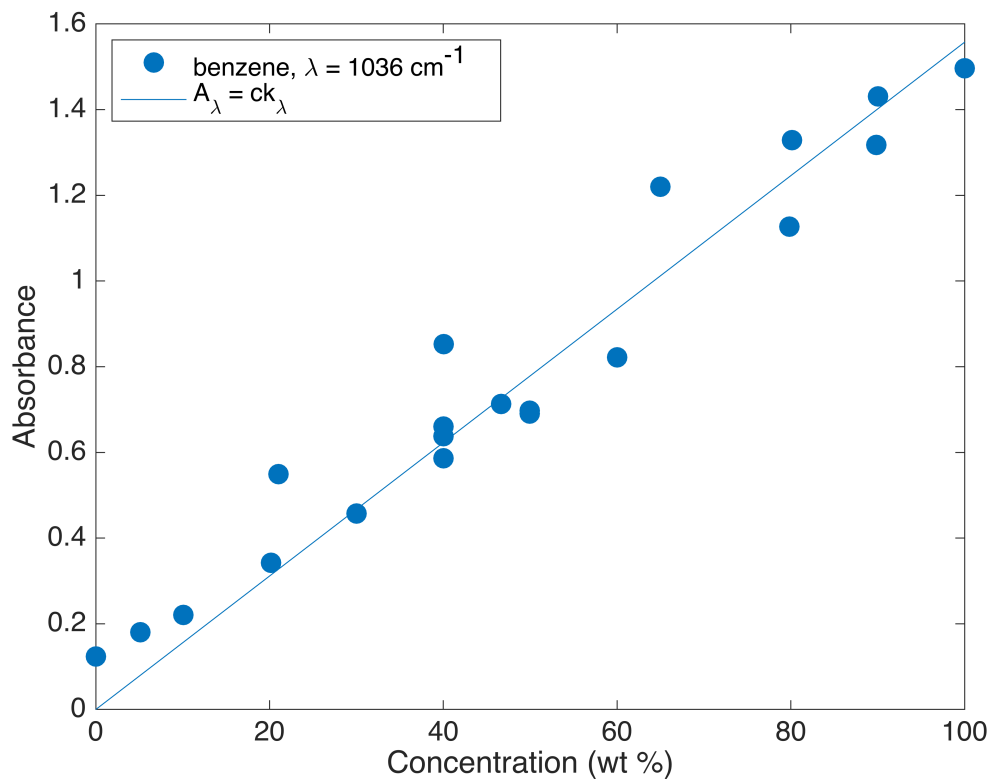
MATLAB's backslash operator computes the least-squares solution to  $c_{\text{benzene}} \cdot k_{\lambda} = A_{\lambda}$ .

```
k_lambda = c_benzene \ A_lambda
```

```
k_lambda = 0.0156
```

Plot the measured absorbance vs the least-squares best fit  $A_{\lambda} = ck_{\lambda}$ .

```
figure;
plot(c_benzene,A_lambda, '.', 'MarkerSize',35)
colorOrder = pnnl_colorOrder(1);
hold on
plot(c_benzene, c_benzene*k_lambda, 'Color',colorOrder(1,:))
legend(sprintf('benzene, \\lambda = %d cm^{-1}',round(lambda)), 'A_\\lambda = ck_\\lambda')
xlabel('Concentration (wt %)')
ylabel('Absorbance')
set(gca, 'FontSize',14)
```



## Choose peaks for the remaining constituents

Choose bands for each constituent that meet the following criteria:

1. High intensity
2. Don't have high overlap with bands from other constituents.

The following bands for benzene, polystyrene, and gasoline, respectively, met those criteria, but we did not do an exhaustive search. There might be others that are more optimal.

```
wavenumber_index = [175, 468, 1128];
wavenumbers_of_interest = Wavenumbers(wavenumber_index)
```

```
wavenumbers_of_interest = 1×3
103 ×
    1.0356    1.6006    2.8734
```

Plot the chosen peaks in each spectra.

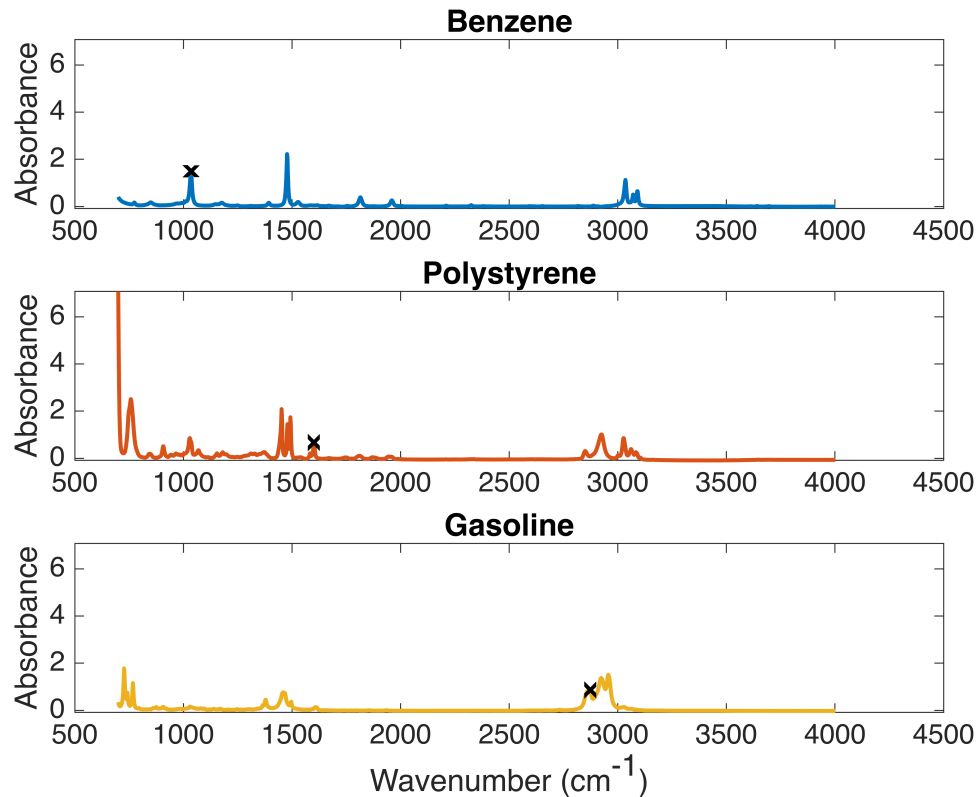
```
n = size(C_train,2);
colorOrder = pnnl_colorOrder(n);
figure;
h = gobjects(1,n);
for j = 1:n
    h(j) = subplot(n,1,j);
    plot(Wavenumbers,A_pure(j,:), 'LineWidth',2, 'Color',colorOrder(j,:));
```



```

hold on
plot(Wavenumbers(wavenumber_index(j)),A_pure(j,wavenumber_index(j)),'xk','MarkerSize',10)
title(ConstituentNames{j})
ylabel('Absorbance')
end
linkaxes(h)
xlabel(WavenumberLabel)
set(h,'FontSize',14)

```



## Repeat for each of the other spectra

Repeat the process for computing extinction coefficients  $k_\lambda$  for each of the other spectra and plot the results.

```

k_lambda = zeros(1,n);
for j = 1:n
    k_lambda(j) = C_train(:,j) \ A_train(:,wavenumber_index(j));
end

```

The extinction coefficients are for benzene, polystyrene, and gasoline respectively.

k\_lambda

```

k_lambda = 1x3
    0.0156    0.0077    0.0098

```

## Cross Validation

Cross-validate by running CLS for each of the rows in the training set, leaving one row out, and using that row as the unknown data.

```
p = size(C_train,1);
C_cross_validation = zeros(p,n);
for i = 1:p
    for j = 1:n
        C_cross_validation(i,j) = pnnl_cls(A_train([1:i-1,i+1:p],wavenumber_index(j)),...
    end
end
```

## Compute Root Mean Square Errors

```
RMSEC = zeros(1,n);
RMSECV = zeros(1,n);
RMSEP = zeros(1,n);
for j = 1:n
    RMSEC(j) = pnnl_rmse(A_train(:,wavenumber_index(j))/k_lambda(j), C_train(:,j));
    RMSECV(j) = pnnl_rmse(C_cross_validation(:,j), C_train(:,j));
    RMSEP(j) = pnnl_rmse(A_unknown(:,wavenumber_index(j))/k_lambda(j), C_validation(:,j));
end
pnnl_display_rmse("Beer's Law",ConstituentNames,RMSEC,RMSECV,RMSEP)
```

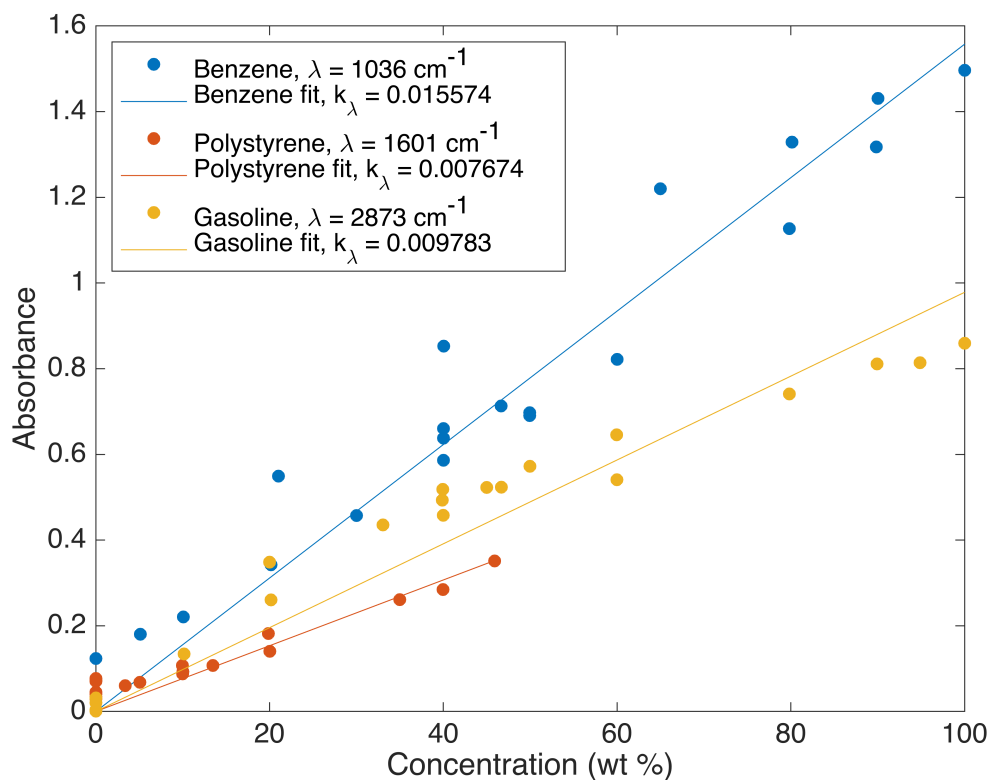
-----			
Beer's Law	Benzene	Polystyrene	Gasoline
RMSEC	6.9805	5.6428	8.2886
RMSECV	7.3288	5.6911	8.8853
RMSEP	11.019	2.753	25.521
-----			

## Plot the results

Plot the results with lines of best fit.

```
figure;
colorOrder = pnnl_colorOrder(n);
legend_string = cell(1,2*n);
legend_number = 0;
for j = 1:n
    plot(C_train(:,j),A_train(:,wavenumber_index(j)),'o',...
        'MarkerEdgeColor',colorOrder(j,:),...
        'MarkerFaceColor',colorOrder(j,:),...
        'DisplayName',sprintf('%s, \lambda = %d cm^{-1}',ConstituentNames{j},round(wa
    hold on
    plot(C_train(:,j), C_train(:,j)*k_lambda(j),'Color',colorOrder(j,:),...
        'DisplayName',sprintf('%s fit, k_{\lambda} = %f',ConstituentNames{j},k_lambda
end
legend('Location','northwest')
xlabel('Concentration (wt %)')
ylabel('Absorbance')
```

```
set(gca, 'FontSize', 14)
```



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